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# Morphology and origin of dolomite in paleosols and lacustrine sequences. Examples from the Miocene of the Madrid Basin

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ABSTRACT

The northern Madrid Basin contains paleosols and lacustrine sequences composed of ordered dolomite. Smectite-rich mudstones with analcime deposited in distal alluvial fans affected by pedogenic processes. Mudstones contain dolomite and silica laminae interpreted as mineralized root-mats. Dolostones with prismatic structure constitute Stage III dolocretes. Homogeneous lacustrine dolomudstones show some features indicative of subaerial exposure. Dolomite textures include: microcrystalline dolomite, coarse crystalline mosaics located in root cavities, dolomite dumbbells and dolomite spheroids replacing clays, dolomudstones or opal. Mol values of $MgCO_3$ of dolomites vary between 47.67% and 53.34% mol. $\delta^{18}O$ values range between −3.65 and −5.51‰ VPDB. $\delta^{13}C$ values range between −7.19 and −8.38‰ VPDB.

Dolomicrite formed in alkaline lakes by direct precipitation and replacement of clays in soils. The rhizosphere was favorable for dolomite mosaic and dumbbells formation. Spheroidal dolomite replaced clays and opal under early phreatic diagenesis. Trioctahedral smectites, silica and analcime indicate that these pedogenic and lacustrine environments were alkaline. Smectites and/or carboxyl groups acted as a catalyst favoring the incorporation of Mg into dolomite. In these non-saline settings the kinetic barriers for dolomite precipitation lowered by high pH and Mg enrichment. Ordered dolomite formation occurred under biogenic and abiogenic conditions, during sedimentation, pedogenesis and early diagenesis.

## 1. Introduction

Since Dolomieu (1979) description of dolomite, its origin has been one of the preferred topics of sedimentary geology. Most dolomites occur in marine sequences by replacement of limestones. The possibility of primary precipitation of dolomite (Last, 1990; Last et al., 2010; Last et al., 2012) has rarely been considered. In the last decades, dolomite has been found in contexts which include the purely continental (Colson and Cojan, 1996; Martín-Pérez et al., 2012). Several experimental studies synthesized dolomite at ambient temperatures (Vasconcelos et al., 1995; Rivadeneyra et al., 2006). In these experiments microbes modified the chemistry of the solution and provided suitable surfaces for nucleation of a poorly-ordered, Ca-rich dolomite (Van Lith et al., 2003; Sánchez-Román et al., 2008). Also it has been shown that dolomite may form abiotically by the catalytic effect of carbohydrates (Zhang et al., 2012), or that carboxyl groups may act as seeds for nucleation of abiotic ordered dolomite (Roberts et al., 2013). Of special interest is the formation of Mg-rich spheroidal carbonates, such as HMC and dolomite, which seems to be favored by the high viscosity of the growth media and high gradients of oversaturation (Fernández-Díaz et al., 2006; Sánchez-Navas et al., 2009). In short, up to now in experimental studies a wide variety of mechanisms have been postulated as producing different types of dolomite, although the results may not be easily applied to the study of the sedimentary record. In this paper we present a detailed study of different types of dolomites formed in a closely-constrained alkaline and Mg-enriched sedimentary/pedogenic/diagenetic environment. The aims of our study are to discuss the wide variety of formation mechanisms and controls (biogenic or non-) of ordered dolomite in pedogenic and lacustrine deposits, and to provide a clue as to the interpretation of micrite and spheroidal dolomites found in ancient sedimentary sequences. In doing so, we try to show that if kinetic barriers for dolomite formation are lowered, dolomite may form by direct precipitation or replacement. The contributions of biotic and abiotic processes play important roles but are not easily distinguished, as both may interplay together.

## 2. Geological and paleo-environmental setting

Sediments analyzed in this paper correspond to Miocene deposits of the northern Madrid Basin in central Spain (Fig. 1A). The basin is filled by continental sediments ranging in age from Paleogene to Pliocene. Paleogene rocks crop out only at the margins of the basin. Miocene deposits have been divided into Lower, Intermediate and Upper Miocene

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Units (Junco and Calvo, 1984; Alonso-Zarza et al., 2004). Boundaries between units are marked by paleo-karstic surfaces (Cañaveras et al., 1996; Rodríguez-Aranda and Calvo, 1997).

Lower and Intermediate Units show concentric arrangement of facies, from coarse basin alluvial deposits to central-area lacustrine carbonates and evaporites, suggesting a geomorphically- and hydrologically-closed basin during sedimentation. The Upper Unit comprises detrital and carbonate sediments mainly deposited in the central and eastern basin. This distribution was interpreted as the result of a change from compressive to extensional regional stress (De Vicente and Muñoz-Martín, 2013) partially opening the basin (Cañaveras et al., 1996).

Carbonate deposits studied are located at the base of the Intermediate Unit in Paracuellos de Jarama area (Madrid) (Fig. 1B). In this area the arkosic alluvial fan transition to lake environments (Alonso et al., 1986) is a belt of carbonate paleosols on arkosic sands, fine loose gravels and brown clays, usually organized in fining-upward sequences (Alonso-Zarza et al., 1992a).

## 3. Techniques and methods

Forty-one samples of carbonates and clays were collected from two outcrops of the Miocene deposits in the northern Madrid Basin of Central Spain (see Fig. 1 for localization). For the description of the samples in the outcrop has followed the description of paleosols, proposed by Retallack (1988). Due to fragility, before cutting and polishing, samples were embedded in resin containing Epofer EX 401 and Epofer 432 in a vacuum system. Conventional optical petrography studies were performed on 44 thin sections. An Olympus BX51 optical microscope with an Olympus U-TVO.5XC-3 built-in camera was used for our study. Olympus cell B© software was used to take photographs.

Whole-rock mineralogy of 28 samples was studied out with a Philips PW-1710 X-ray diffraction (XRD) system operating at 40 kV and 30 mA, under monochromatic CuKα radiation. Mineralogical characterization of the richer clay sample was carried out on oriented aggregate samples of <20 μm fraction (separated by sedimentation) using oriented air-dried slides that were ethylene glycol solvated and heated to 550 °C (Brindley, 1961). Quantitative analysis was performed by Chung (1975) procedure using EVA software by Bruker. In the powder of samples, the <20 μm fraction measured using the 060 reflections between 60.50 and 61.50° 2θ to confirm the presence of trioctahedral minerals.

The percentage mole values of $MgCO_3$ were determined following Scholle and Ulmer-Scholle (2003), after Goldsmith et al. (1961). The degree of ordering of dolomite was determined from diffraction, with correlation between intensity of (015) and (110) peaks measured according to standard procedures (Hardy and Tucker, 1988).

SEM observations were carried out on gold-coated samples using three microscopes: 1) JEOL JSM-6400 of the ICTS-CNME Luis Brú of Complutense University of Madrid (Spain) working at 20 kV, 2) JEOL JSM-820 of the CAI of geological techniques of Complutense University of Madrid (Spain) working at 20 kV and 3) FEI QUANTA 200 apparatus of the MNCN Laboratories working at 30 kV.

A wavelength dispersive electron probe microanalyzer (WDS-EPMA), model JEOL JXA 89000, was used to determine the proportions of the main elements in the various minerals. Analyses were performed on gold-coated, polished thin sections.

The $\delta^{13}C$ and $\delta^{18}O$ values from 17 selected powdered samples were obtained by the Scientific and Technical Survey in Barcelona University (Spain). Samples were washed with 100% phosphoric acid at 70 °C for

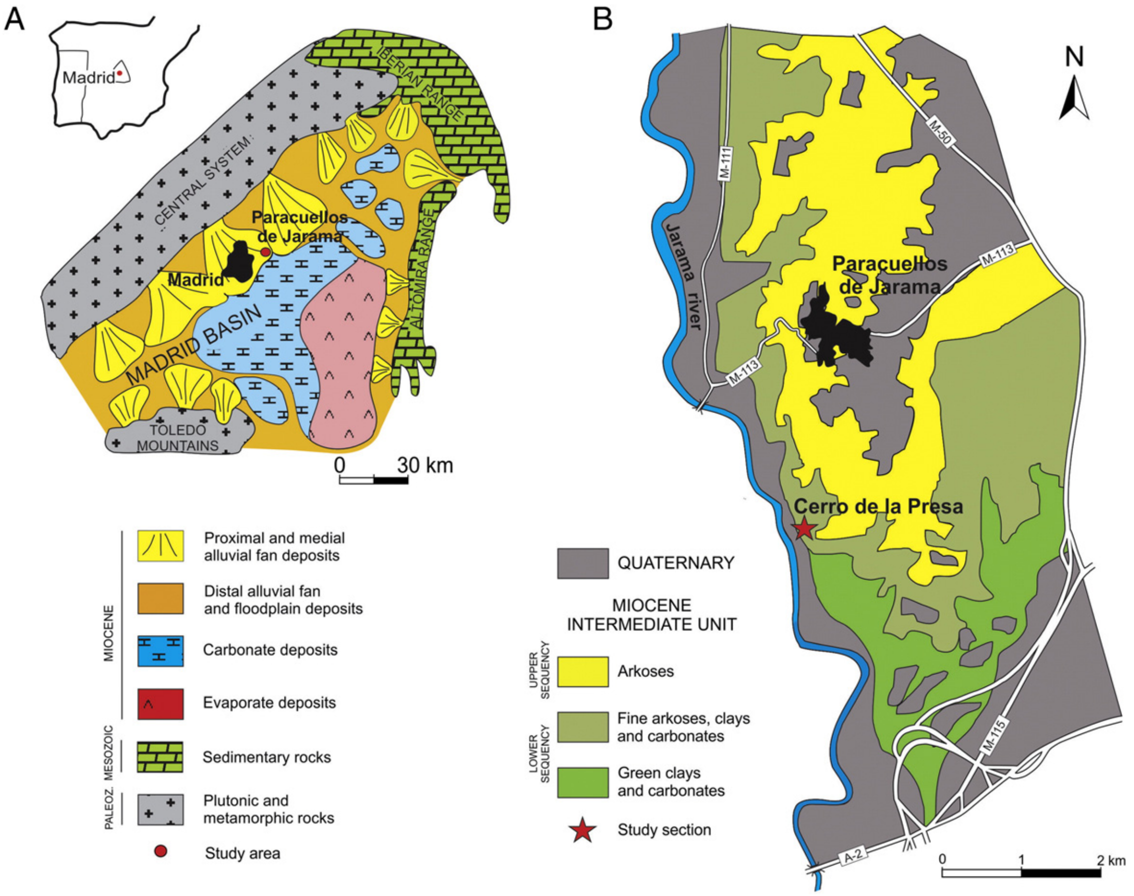

**Fig. 1.** A) Location of the study area (Paracuellos de Jarama) in the palaeogeographic context of the Madrid Basin of Spain during the sedimentation of the Intermediate Unit. B) Map Miocene units and situation of the study section, within the Paracuellos de Jarama area.